Processing of Blue Boron Nitride Thin Films with a Solid–Gas Reaction

Mohamed Mokhtari, Hyung S. Park, Herbert W. Roesky,* Stephen E. Johnson, Wolfgang Bolse, Jens Conrad, and Winfried Plass

Dedicated to Professor Rudolf Taube on the occasion of his 65th birthday

Abstract: For the first time, solid–gas reaction techniques have been used for the synthesis and processing of thin films of boron nitride. Clear to intensely colored blue BN films were grown on Si(100) substrates by the transformation of borazine ($B_3N_3H_6$) with a titanium complex as initiator under flowing nitrogen gas. The thickness of the films ranged from 70 to 100 nm, as determined by Rutherford backscattering (RBS) and atomic force microscopy (AFM) analyses. The intensity of the blue color of the thin film can be correlated to its thickness. The composition of the film determined by RBS studies corresponds to the stoichiometric formula $B_{0.49}N_{0.45}O_{0.06}$, and N/B and O/B ratios are found to be 0.92 and 0.12, respectively. Nitrogen contents determined by nuclear reaction analysis agree well with the RBS results. Moreover, Auger electron spectroscopy (AES) measurements show that no titanium is present in the films and confirm the composition determined by RBS studies. X-ray photoelectron spectroscopy (XPS) shows the presence of boron and nitrogen in the blue BN film. Electron spin resonance (ESR) experiments at 293 and 12 K indicate a single broad signal with a g value (g = 2.005) close to that of a free electron. This synthetic approach provides opportunities for the preparation of new thin-film materials and for the fundamental study of solid–gas reactions.

Keywords
borazine · boron nitride · materials science · thin films · titanium complexes

Introduction

Boron nitride is a widely studied material owing to its unique combination of properties, such as low density, high melting point, thermal conductivity, chemical inertness, and high electrical resistivity.[1, 2] It is extensively used, both as bulk material and as thin films in electronic devices and ceramic applications, including crucible technology, high-temperature insulators, optically transparent substrates for X-ray lithography masks, and coatings.[3] Traditionally, routes to boron nitride have involved classical high-temperature syntheses,[4, 5] such as reaction of boron with nitrogen, metal borides with ammonia and nitrogen, and metal borohydrides with ammonium chloride (under N_2) at temperatures above 1500 °C.[1] Thin films of BN have been the subject of many studies and have been prepared by a variety of techniques, including chemical vapor deposition (CVD).[1, 6] In practise, the most widely used precursors in CVD method are BCl_3/NH_3 and $BCl_3/NH_3/H_2$ mixtures. BN films are normally obtained at temperatures above 1000 °C.[1] Boron nitride thin films have also been produced by plasma-enhanced CVD,[7] pulsed laser deposition,[8, 9] r.f. magnetron sputtering,[10] and hot-filament CVD.[11]

In addition to the methods outlined above, there is a great interest in polymeric preceramic compounds that yield BN.[12] However, many of the potential molecular precursors to BN contain organic groups, which are possible sources of carbon contamination in boron nitride. Considerable interest is therefore currently being shown in the pyrolysis chemistry of borazine ($B_3N_3H_6$) as a potential molecular precursor to BN.[1, 13] In this paper we report on a facile and new solid–gas reaction method for the preparation and processing of boron nitride thin films. There have been no previous reports of experimental studies on using a solid–gas reaction to produce a blue BN film.

We have deposited blue BN films at relatively low temperatures and have optimized the conditions of the deposition of the films. The transformation of borazine with a titanium complex as initiator was used for deposition of the film on Si(100) substrates. The major aim of the present work is to answer the following questions: How does the titanium function in the process? What is the exact composition of the film? To answer these questions, we characterized the blue films of BN by a variety of surface analytical techniques.

Results and Discussion

Preliminary experiments were carried out to optimize the temperature range (300–800 °C) for deposition of the blue BN films. Intense, blue films were observed which initially appeared

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at 550 °C. The optimal temperature for growing the highest quality films was 700 °C with a reaction time of 1 hour. These conditions correlate with those used in the well-known conversion of borazine to the hexagonal structure by thermal decomposition.[14] Recent papers have reported the preparation of amorphous boron nitride from the reaction of haloborazine $B_3X_3N_3H_3$ (X = Cl, Br) with alkali metals (K, Rb, Cs). The amorphous product converted to the partially ordered turbostratic form of boron nitride at 1100 °C.[15] Borazine can also be dehydropolymerized to give polyborazylene. Pyrolysis studies showed that the polymer is converted to boron nitride by heating to 900–1450 °C.[16] In both cases cited above a white boron nitride powder was observed, whereas we observed the surprising blue color of BN films. This color was observed on both sides of the Si(100) substrate and in the platinum crucible. Moreover, the blue color did not vary with the viewing angle. This suggests that its origin is not related to structural interference. The titanium complex $[TiCl_4(NH_3)_4]$ as an initiator is essential for the formation of the blue BN thin film. Alternatively, $[(NH_4)_2TiCl_6]$ can function as an initiator, however, impurities of H_2O afford thin films contaminated with appreciable amounts of oxygen. The role of the titanium reagent in the reaction is intriguing and required examination. In the past the synthesis of cubic boron nitride has been studied by using magnesium powder as a typical catalyst.[17] However, in this case very high static pressures (> 100 kbar) and temperatures (> 3000 °C) were required to convert hexagonal boron nitride to cubic boron nitride. Moreover, it is known that hexagonal BN films can be prepared from borazine.[18]

In order to understand the role of titanium complex, control experiments were performed under the optimal conditions cited above. Borazine alone afforded a characteristic white boron nitride film; no blue color was observed. $[TiCl_4(NH_3)_2]$ gave thin films of TiN.[19] This result strongly supports the premise that the titanium complex initiates the formation of blue BN thin films.

The blue BN films were characterized by a combination of surface analytical techniques. A number of films (ca. 10) were analyzed by RBS method. Although the film thickness varied between 70 and 100 nm, as measured by RBS and AFM methods, all films exhibited the same blue color. Figure 1 shows a photograph of a typical BN film deposited on a Si(100) substrate. The surface of the film exhibits a characteristic blue color, is very smooth, and shows a strong reflectivity. Under the conditions described, film formation is straightforward to reproduce.

Abstract in German: *Es wird erstmals über die Herstellung von dünnen Bornitrid-Schichten durch eine Feststoff-Gas-Reaktion berichtet. Als Ausgangsverbindung diente Borazin, das durch einen Stickstoffstrom über einen Titan-Komplex überschichteten Si(100)-Träger geleitet wurde und unter Zersetzung farblose bis intensiv blaue BN-Schichten lieferte. Die Schichtdicken von 70–100 nm wurden sowohl mit Rutherford-Streustrahlung (RBS) als auch rasterkraftmikroskopisch (AFM) charakterisiert. Die Farbintensität der blauen Schichten kann auf die Schichtdicke zurückgeführt werden. Die Zusammensetzung der Schichten entspricht der Formel* $B_{0.49}N_{0.45}O_{0.06}$. *Das N/B- und das O/B-Verhältnis wurden mit RBS bestimmt (0.92 bzw. 0.12) und durch eine Kernreaktionsanalyse bestätigt. Des weiteren ergaben Auger-Elektronen-spektroskopische (AES) Messungen, daß kein Ti in der Schicht vorliegt, was durch entsprechende RBS-Untersuchungen bestätigt wurde. Durch Röntgen-Photoelektronen-Spektroskopie (XPS) kann auf das Vorhandensein von B und N in den Filmen geschlossen werden. Die Elektronen-Spin-Resonanz (ESR) zeigt bei 293 und 12 K ein breites Singulett (g = 2.005), welches nahe dem des freien Elektrons liegt. Die hier beschriebene Methode zeigt sowohl die Möglichkeiten zur Herstellung neuer Schichtmaterialien als auch grundlegende Untersuchungen zu Feststoff-Gas-Reaktionen.*

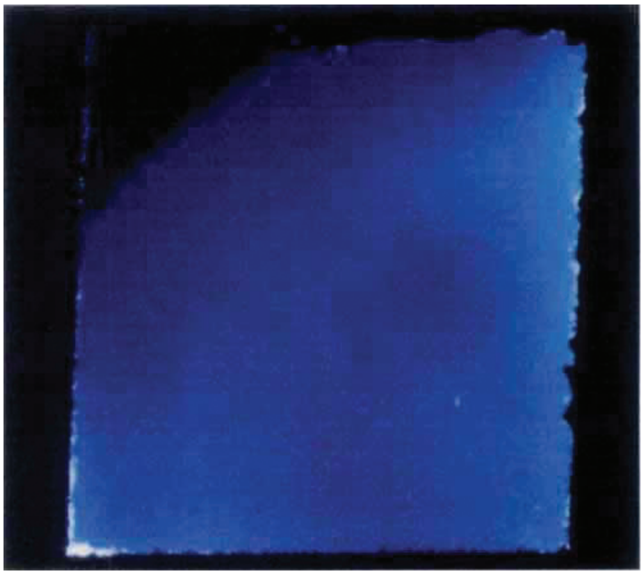

Fig. 1. Photograph of blue BN film (deposited on a Si(100) substrate).

RBS analyses were used to identify the composition of the films. A typical RBS spectrum of the blue BN film on Si(100) is shown in Figure 2a. The RBS yield of the film components (B, N, and O) is superposed by that of the Si backing. However, the latter could be fitted with a polynomial of degree 3 and subtracted from the data. The resulting spectrum is shown in Figure 2b. The solid line represents a simulation performed by means of the RUMP code,[20] assuming a film composition $C_B = 49(2)$, $C_N = 45(2)$, and $C_O = 6(2)$ atom %, and perfectly fits the experimental data. The atomic ratios of nitrogen, boron, and oxygen were found to be N/B = 0.92 and O/B = 0.12. In addition a thin carbon film of a few nm thickness was found to cover the sample, which was probably deposited during RBS analysis. The Ti concentration in the film was of the order of the detection limit ($C_{Ti} < 0.5$ atom %). A comparison of the N/B and O/B atomic ratios of blue BN films with those of CVD BN obtained by AES analysis[21] and dip-coated BN obtained by AES and XPS analyses[3] is shown in Table 1. The composition of the blue BN film has also been confirmed by resonant nuclear reaction analysis utilizing the $^{15}N(p,\alpha\gamma)$ nuclear resonance at E_R = 430 keV.[22] The γ-ray yield as a function of the proton beam energy is shown in Figure 3 and is compared with the profile

Table 1. Comparison of N/B and O/B atomic ratios of blue BN with that of CVD BN and dip-coated BN.

	Blue BN	CVD BN [a]	Dip-coated BN [b]
N/B atomic ratio	0.92	0.7	0.6–0.8
O/B atomic ratio	0.12	0.2	0.1–0.25

[a] Ref. [21]. [b] Ref. [3].

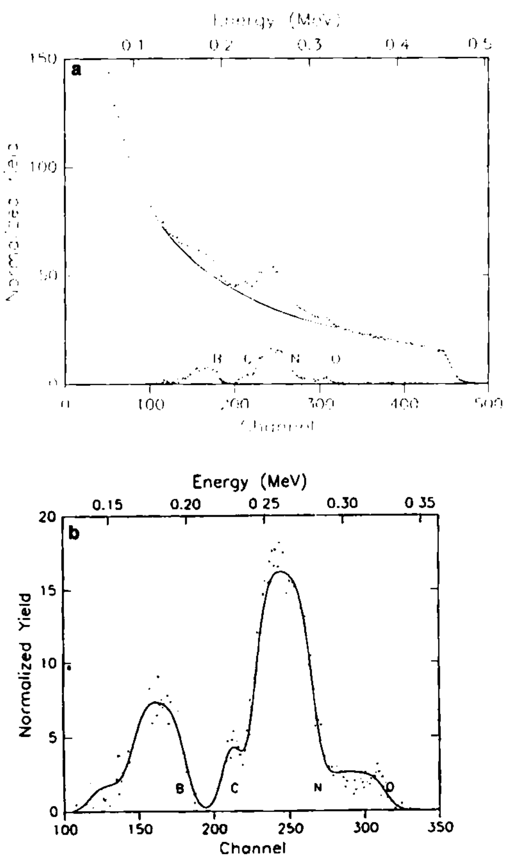

Fig. 2. a) Typical RBS spectra of the blue BN film (deposited on Si(100)). b) Same as a) after subtracting the Si background using a polynomial of degree 3. The solid line represents the RUMP simulation of the composition described in the text.

measured for a TiN film on Si. By using the latter as a standard for $C_N = 50$ atom%, the theoretical γ-ray yield for a $B_{0.49}N_{0.45}O_{0.06}$ compound can be calculated according to Equation (1), where N_γ^{TiN} denotes the γ-ray yield measured for

$$N_\gamma^{BNO} = N_\gamma^{TiN}(C_N^{BNO}/C_N^{TiN})(\varepsilon_p^{TiN}/\varepsilon_p^{BNO}) \quad (1)$$

TiN; C_N^{BNO} and C_N^{TiN} are the nitrogen concentrations in the $B_xN_yO_z$ compound and in TiN, respectively; ε_p^{BNO} and ε_p^{TiN} are the stopping powers for protons in the $B_xN_yO_z$ compound and in TiN. The result, indicated by an arrow in Figure 3, agrees perfectly with the experimental value and confirms the composition measured by RBS.

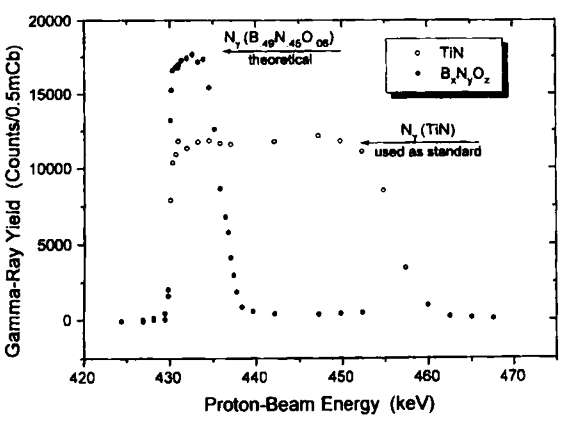

Fig. 3. γ-Ray (4.439 MeV) yield obtained for a blue BN film on Si(100) as function of the proton beam energy. For comparison, that obtained for a TiN film on Si is shown, which was used as a standard for $C_N = 50$ atom%. The theoretical γ-ray yield for the layer composition found by RBS is indicated by an arrow and agrees well with the experimentally observed value.

BN thin films have been examined by AFM as a surface imaging probe, in the contact or tapping modes. Areas ranging from 3000 to 100 nm^2 were imaged. The image reveals a uniform surface with cylindrical type features, indicating a columnar type growth. The cylinders are rather symmetrical, exhibiting a central axis. In the repulsive mode of imaging, the surface of the blue BN films can easily be recognised and is reproducible (Fig. 4). The cylinders shown in Figure 4b have round bases, with diameters ranging from 30–70 nm and heights in the range of 90–140 nm. Profile analyses indicate that the cylinders are symmetrical and display a uniform topography. An average film thickness of 95 nm was observed by AFM measurements. Additionally, the roughness of the substrate and the film on the substrate are given by values of 18.3–20.8 and 2.65–2.69 nm, respectively. The low values of roughness correlate well with the smoothness and uniform topography of the film.

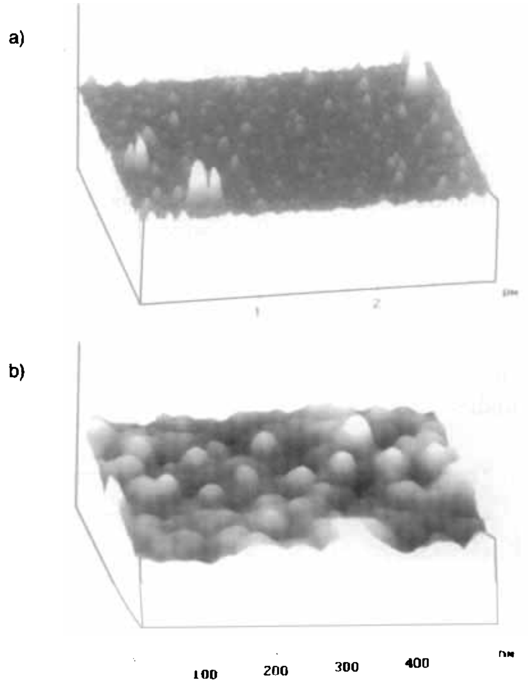

Fig. 4. AFM images (in repulsive mode) of the surface of blue BN film. a) x: 1000 nm/div., z: 45 nm/div. and b) x: 100 nm/div., z: 16 nm/div.

Infrared (IR) spectroscopy was used for additional characterization of the blue BN thin films. Figure 5 shows the IR absorption spectra of the blue BN film (Fig. 5a) and of the Si(100) substrate before the deposition (Fig. 5b) in the region from 2500 to 600 wavenumbers. The BN film exhibits characteristic absorptions (1377.3 (br, s) and 792.2 cm^{-1} (m)), which compare well with the corresponding BN stretching and bending modes of hexagonal BN (1400–1370 and 800–780 cm^{-1}, respectively).[23, 24] No further bands corresponding to Ti–N, Ti–B, or Ti–O stretching and bending modes are present in the spectra. A band at 1107.4 cm^{-1} is characteristic of the Si-O-Si vibration in the substrate.

X-ray diffraction (XRD) of the blue films shows a number of sharp signals of low intensity compared to the Si(h00) reflections, characteristic of diffraction lines in a thin film (< 100 nm). The observed reflections were close to characteristic lines of ASTM h-BN,[25] however, the lines are slightly shifted. In order to further characterize the blue boron nitride thin

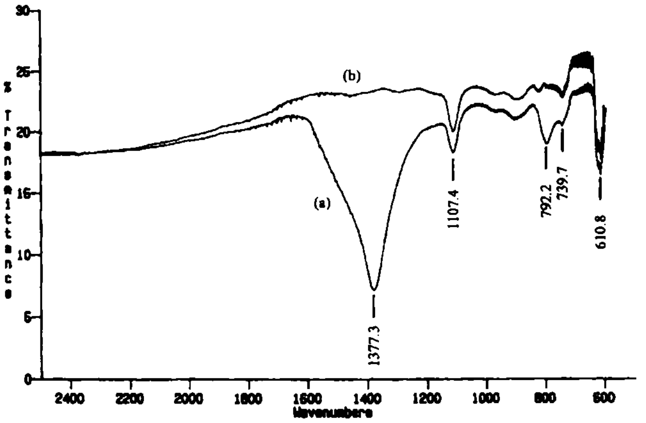

Fig. 5. Infrared spectra of a) blue BN film and b) Si(100) substrate.

films and to confirm the composition obtained by RBS analyses, AES and XPS investigations were conducted. Figure 6 shows the Auger survey spectra containing the principal Auger transition peaks. The depth profile obtained for the film confirms the composition determined by RBS analyses. No titanium is detected in the film. This result is in good agreement with those obtained for the control experiments, and the RBS and IR studies.

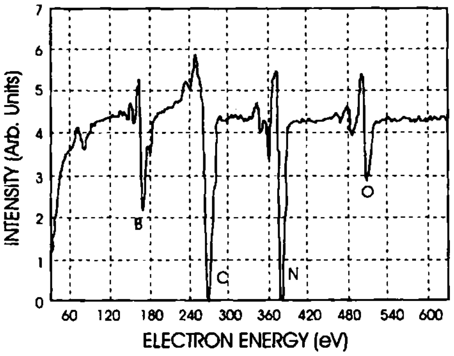

Fig. 6. First-derivative Auger electron survey spectra showing the principal Auger transition peaks of the blue BN film.

XPS analysis, which is a powerful tool for determining the types of bonding in each element, was also performed on the blue BN film. The results indicate the presence of both boron and nitrogen in the film. The B 1s and N 1s peaks of the blue BN film on Si(100) before sputtering are fitted onto a curve in Figure 7. Sharp peaks are observed at 191.3 eV for B 1s and at 399.0 eV for N 1s. The binding energy of B (191.3 eV) is close to the B 1s signal expected for a B–N bond (190.5 eV).[26] The observed N 1s signal is similar to that observed in h-BN or t-BN (398.5 eV); this suggests that the nitrogen present is indeed bonded to boron.[26] After sputtering (6 min at 500 eV and 6 min at 800 eV), no significant difference is observed; this indicates that the film is stable and not distorted. However, a slight shift for B 1s (192.5 eV) and N 1s (399.7 eV) compared to the peaks of B and N before sputtering is observed. In both cases the slight shift to higher energies (significant increase after sputtering) indicates that there might be some oxonitrides in the form of BO$_x$N$_y$ on the surface and even in the blue BN films. These species are due to small amounts of contaminants.

It is clear that, in any class of material, defects play a role in determining the mechanical, thermal, and electronic properties.

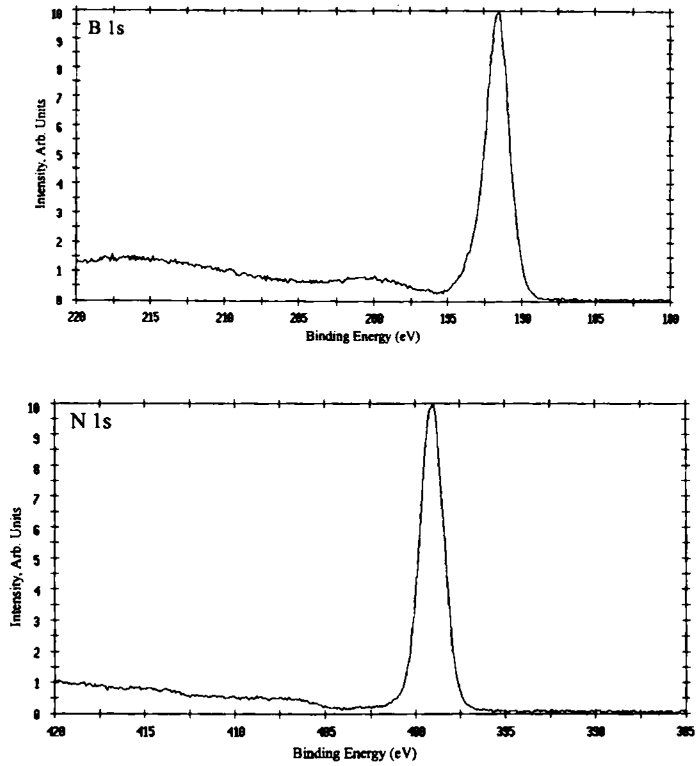

Fig. 7. Curve-fitted B 1s and N 1s peaks of blue BN films on Si(100) before sputtering.

These defects have been investigated by ESR spectroscopy in bulk graphitic BN.[27,28] Two types of paramagnetic centers were observed. One is assigned to an unpaired electron interacting with a single boron atom; the other is due to an unpaired electron interacting with three boron atoms. Nitrogen vacancies and interstitial atoms are also responsible for the observed ESR signals.[29,30] Indeed, during the boron implantation the concentration of nitrogen vacancies increases. The interstitial boron atoms stabilize the unpaired electrons in the nitrogen vacancies, so the concentration of paramagnetic centers increases. Another parameter that could influence the paramagnetic signals in the three allotropic forms of BN is a carbon atom. It has been pointed out by several authors that carbon plays a crucial role in the stabilization of the electron in nitrogen vacancies in graphitic boron nitride.[31,32] Furthermore, interstitial carbon atom could be responsible for the yellow color and paramagnetism in h-BN, and impurities are at least sufficient, if not necessary, for the creation and stabilization of particular defects in the lattice.

The blue BN film was therefore studied by ESR spectroscopy at room and low temperatures. The result at room temperature is shown in Figure 8. As we can see from this figure, the lineshape of the ESR signal is of Lorentz type, and the g value calculated from the ESR spectrum is 2.005, characteristic of a free electron. A signal with the same g value is also observed at low temperature (12 K).

The mechanism of the reaction is not exactly known, but, as we have described previously, the blue color, which can be related to defects in the BN films, is observed only when using both precursors—titanium complex [TiCl$_4$(NH$_3$)$_4$] and borazine (B$_3$N$_3$H$_6$). These results indicate that the titanium complex plays a role comparable to that of the carbon atom in BN films and that it might be responsible for the coloring and stabilizing

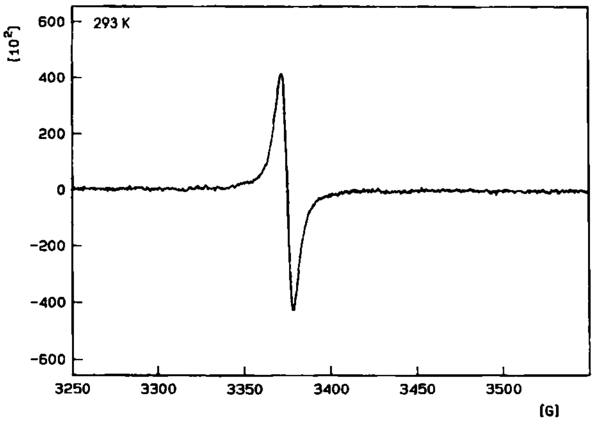

Fig. 8. X-band ESR spectra of blue BN film at 293 K.

defects in the BN films. However, a difference does exist between these two cases. Carbon is present as an impurity in h-BN; the analysis of the chemical composition of the blue BN films by RBS and AES showed that no titanium atoms are found in the film.[33] Moreover, the oxygen contents of BN systems is not responsible for the blue color as has been demonstrated by several groups.[3, 21] Therefore, we assume that during the reaction the titanium complex is decomposed accompanied by an electron transfer to the BN film. This electron is responsible for the paramagnetic signal, while the blue color is probably related to the defects in the BN film caused by the electron doping process.

Conclusion

Our synthetic method, based on the reaction of borazine with a titanium complex as the initiator, consistently affords reproducible blue BN thin films (thicknesses ranging from 70 to 100 nm). The physical properties of the thin films (texture, thickness, surface homogeneity, and particle size) can be controlled by this facile, new method of preparation. To our knowledge, this is the first report of a blue nitride with high reflectivity, which might be used as colored ceramic in the field of materials science. Perhaps, our synthesized BN films, with their very different properties, such as the blue color, the paramagnetic signal, and the electrical conductivity, might prove to be more important than the colorless BN. Preliminary results have already indicated that our method can be extended to other systems. Specifically, a new class of electrically conducting material deposited on a variety of substrates (Si, SiO_2, Al_2O_3) is the principal object of current investigations.

Experimental Procedure

Synthesis: We have studied the deposition of blue BN on Si(100) substrates using borazine [34,35] and [$TiCl_4(NH_3)_4$] [19,36]. The gas–solid reaction was carried out in a reactor shown in Figure 9. A nitrogen flow rate of 12 mL min^{-1} was maintained during the deposition. Silicon substrates (Si(100), dimension: 5 × 5 mm^2) used in the present study were degreased with isopropanol, rinsed with distilled water, and treated with hydrofluoric acid for a few seconds. The substrate was rinsed again with distilled water and then treated with dry nitrogen prior to film deposition. [$TiCl_4(NH_3)_4$], with a characteristic yellow color, was ground to a homogeneous fine powder with particle size in the order of a micrometer. A sample of 0.15–0.25 g of the powder was taken to cover the Si substrate. The layer of powder had a uniform thickness on the surface of the substrate of about 2 mm. Although the amount of complex (thickness of coating) varied, all the films exhibited the same blue color. The Si substrates covered with the titanium complex were placed in the platinum crucible. Finally, the stream of borazine gas was passed through the reaction tube for 1 h, when a temperature of 700 °C was attained. After the deposition was complete the system was cooled to room temperature under nitrogen.

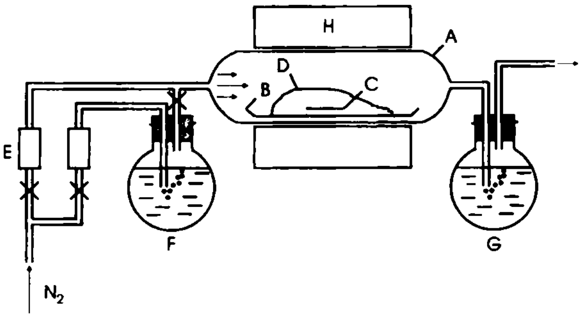

Fig. 9. Schematic representation of the reactor. In the center of an horizontal quartz tube (A) (outside diameter: 27 mm; length: 550 mm), a platinum crucible (B) (length: 50 mm) contains the Si(100) substrate (C) (5 × 5 mm^2) covered with the titanium complex (D). A nitrogen stream, controlled by flowmeters (E), is loaded with borazine (F) and introduced into the reactor. The effluent gases exit the reactor through a bubbler (G). Prior to the deposition, the tube was purged with dry nitrogen gas (15 min) and subsequently heated in an oven (H).

RBS Measurements: Rutherford backscattering spectroscopy was used to analyze the depth distribution of elements in the films. A comprehensive description of the RBS technique has been reported [37]. Details concerning the present setup are described in ref. [38]. The RBS experiments were carried out at the Göttingen 500 kV ion implanter IONAS [39] at room temperature with 900 keV α particles under normal incidence. The backscattered α particles were detected by two Si surface barrier detectors at scattering angles of 165°. The detector resolution of typically 13 keV (FWHM) was the effective limitation on the depth resolution $\Delta X \approx 10$ nm, since the FWHM of the α beam is less than 0.3 keV [39] and straggling inside the sample is about 2–3 keV [40]. The spectra were modeled with the computer simulation program RUMP [20].

RNRA analysis: Resonant nuclear reaction analysis utilizing the $^{15}N(p,\alpha\gamma)^{12}C$ resonance at $E_r = 429.57(9)$ keV, ($\Gamma_r = 124(17)$ eV, $E_\gamma = 4.439$ MeV) was used to determine the absolute nitrogen contents in the blue BN films. The 4.439 MeV γ-ray yield N_γ, determined as a function of the energy E_0 of the incident monochromatic proton beam, is a measure of the ^{15}N concentration $C_N = N_\gamma \varepsilon / k$ at a depth $X(E_0) = (E_0 - E_R)\varepsilon\rho$. ε denotes the proton stopping power of the compound and ρ its atomic density. k only depends on the absolute detector efficiency and the resonance strength. A detailed description of the technique has been published elsewhere [41].

AFM analyses: Atomic force microscopy was performed on a Nanoscope III (Digital Instrument, Santa Barbara, CA, USA). Head types E and J; E, X: 28.1 nm V^{-1}, Y: 31.0 nm V^{-1}, Z: 5.60 nm V^{-1}; J, X: 328 nm V^{-1}, Y: 377 nm V^{-1}, Z: 11.6 nm V^{-1}; 256 × 256 points; E_{max}: X: 12364 nm, Y: 13640 nm, Z: 2462 nm; J_{max}: X: 144320 nm, Y: 165880, Z: 5104 nm; asymmetric Si tips with 17 and 25° vertex angles; cantilever with spring constant 23–92 N m^{-1}; images were taken in constant height mode, plane-fit, and low-pass filter. Measurements made on several films were reproducible. Cross-sections were obtained for each sample in the depth-profile analysis. Measurements were made from the base of each peak to its maximum height.

IR Measurements: IR spectra were taken on a BIO RAD FTS-7 IR spectrometer in the region from 600–2600 cm^{-1}. For sp^2-bonded BN (hexagonal graphite-like form), there are two characteristic absorptions at 1370 and 800 cm^{-1} associated with the in-plane BN bond stretch and the out-of-plane B-N-B bond bend, respectively [42]. Absorption spectra were performed on the blue BN film and compared to the spectrum of a Si(100) substrate that was cleaned by the same dipping process as the deposited substrates.

AES Measurements: Auger electron spectroscopy data were obtained with a Physical Electronics PHI 595 scanning Auger spectrometer at a base pressure of 10^{-9} mbar. The spectrometer was equipped with a cylindrical mirror electron energy analyzer (CMA) having an integral, coaxially mounted electron gun. Auger electron spectra were recorded with an energy resolution of 0.5%. Surface composition of the deposited blue BN films were analyzed. An AES depth profile was obtained with a 3 keV Ar$^+$ ion beam (current density 1 μA) over an area of 0.2 × 0.2 mm^2. Such a high current density (1 μA) gives evidence of the electrical conductivity of the blue BN films. For comparison a current density of 0.01 μA was used for a dip-coated BN [3]. The sputtering rate for the blue BN films was estimated to be 1.2 nm min^{-1}.

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XPS Measurements: X-ray photoelectron spectroscopy studies were conducted by Dr. M. Neumann and S. Bartkowski at the Department of Physics, University of Osnabrück (Germany). An ESCA spectrometer of Perkin-Elmer PHI 5600 ci, with monochromated Al_{K_α} radiation was used. The spectrometer was equipped with a 0.8 keV Ar^+ sputter gun and the electron-energy analyzer was calibrated to the Au $4f_{7/2}$ line at 84 eV. The resolution of the concentric hemispherical analyzer was adjusted to less than $\Delta E = 0.4$ eV. The power used was 250 W, and the base pressure in the sample chamber was 5×10^{-9} mbar during data collection. The spectrometer was also equipped with an electron flood gun, which provided a low flux of electrons to compensate for sample charging. Low-resolution broad scans were collected at a pass energy of 187.85 eV and a spot size of 800 µm to identify the elements of the blue BN film over a range of energy of 1400 eV. Higher resolution spectra were collected at a pass energy of 23.5 eV to obtain more detailed chemical information for the blue BN film. Due to the conducting character of the film it was not irradiated by the electron beam charge neutralyzer during the measurements.

ESR Measurements: Electron spin resonance studies were recorded at 293 and 12 K with a Bruker ECS 106 spectrometer using a temperature device from Oxford Instruments (ESR 900). The *g* values are given relative to dpph (2,2-diphenyl-1-picrylhydrazyl), and standard spectrometer settings are as follows: microwave frequency 9.48 GHz, microwave power 200 mW, modulation amplitude 1.3 G, receiver gain 5×10^4, scan range 140 G, scan time 42 s.

Acknowledgements: M. M. thanks the EU for a post-doctoral fellowship (contract ERBCHBGCT 930338). We are thankful to the National Science Foundation and the Deutsche Forschungsgemeinschaft for support of this work. We are grateful to the following colleagues who have contributed to this study by providing physical measurements: S. Bartkowski, K. Keller, Dr. L. Martinez, Dr. M. Neumann, Dr. A. Perrin, Dr. C. Perrin, Prof. A. Reller.

Received: December 27, 1995 [F 274]
Revised: May 23, 1996

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